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著者	YOH　Muneoki
journal or publication title	Journal of Integrated Field Science
volume	9
page range	53-57
year	2012-03
URL	http://hdl.handle.net/10097/54441

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Keywords: nitrogen discharge, river, ground water, anthropogenic N loading, sink of nitrogen, denitrification

Received 14 December 2011; accepted 5 January 2012

Abstract

Large apparent N loss has often been observed between the anthropogenic N input and the riverine N export in river basin, but few persuasive results are available to verify its cause. Here, both a hilly agricultural area and an upland-lowland transect are studied to clarify the implication of groundwater denitrification that could account for the NO_3^- removal during discharge process. In a sloping highland used for cabbage agriculture, the estimated NO_3^- concentration calculated from the N and hydrological budgets agreed well with observed NO_3^- concentration in streams, indicating that the stream NO_3^- concentration can be simply accounted for by the N and water balance and negligible denitrification in this hilly region. In contrast, decreased NO_3^- concentrations are invariably observed in lower sites of slope, where more humid condition prevails. A transect study in an agricultural region showed marked decreases in NO_3^-/Cl^- ratio and dissolved oxygen concentration and significant increases in dissolved N_2/Ar ratio in ground water in lowland sites, clearly indicating NO_3^- removal by denitrification. Forest sites having a groundwater table shallower than ca. 1m also tend to have evidence of denitrification and other reductive processes. Except sloping areas, water is due to move through the groundwater in the lowland before flowing out to rivers, where reductive condition prevails. From the reasons raised here, it is highly likely that a large part of nitrogen discharged from land surface may be removed by denitrification especially in the river basin scale.

Introduction

The increase of N loading from anthropogenic sources such as agriculture, sewage, and atmospheric deposition have resulted in the increase in nitrogen concentration in river discharge. Increased riverine N export is expected for catchments having large N load such as in European and Eastern Asian countries (Seitzinger and Kroeze, 1998). A linear relationship has often been shown between the net areal N input and the riverine N flux even for large river basins (Howarth et al., 1996).

But importantly, the observed N output by river discharge is much less than the calculated N input: regional nitrogen fluxes in rivers are only 16% to 25% of the total of anthropogenically derived nitrogen inputs (Howarth et al., 1996; Caraco and Cole, 1999; Howarth et al., 2006). The discrepancy between N load and riverine N export suggests a significant sink in river basins. Denitrification in wetlands and aquatic ecosystem has been considered important, but it is also thought that other mechanisms such as storage in soil and forests could be of importance as well. Large uncertainty remains as to the cause of this nitrogen loss with little robust evidence showing the contribution of denitrification in the watershed scale. It is essential to understand the biogeochemical behavior of N after anthropogenic loading to environments including this large possible sink. The present paper discusses the potential importance of denitrification, which likely acts as a significant sink to remove dissolved nitrogen during the process of discharge especially in lower reaches of rivers.

Materials and method

N budget was studied in an agricultural highland area, Tsumagoi, Gumma Prefecture, where agricultural field, mostly for cabbage, is distributed in hilly landscapes around 1000 – 1400 m asl. It is conceivable that groundwater would be mostly well-oxygenated due to relatively fast flowing in this sloping region. River water sampling was conducted in June, August and October, 2005, at 28 fixed tributaries and 10 fixed mainstream points of the Agatuma River. Concentration of nitrate and total dissolved nitrogen was measured by an ion chromatography (Dionex, DX-120) and a total nitrogen analyzer (Mitsubishi Chemical Analytech, TN-100), respectively. The average concentration was used for the analysis.

The watersheds have variable land coverages of cabbage field, forest, and others. The nitrogen loading into a watershed was calculated from the following equation, on the assumption that the leaching from cabbage fields is the sole source of dissolved nitrogen.

$L = (F - H) \times A$

where L, F, H, and A are N loading into a watershed (kg N $ha^{-1}year^{-1}$), the fertilizer application rate to cabbage field (180 kg N $ha^{-1}year^{-1}$; Japan Agricultural Cooperatives at Tsumagoi village), N recovery due to cabbage harvest, and the areal coverage of cabbage field in a watershed, respectively. The N recovery by cabbage harvest (H) was calculated from the typical cabbage yield (6.23×10^4 kg ha^{-1} yr^{-1}; Japan Agricultural Cooperatives at Tsumagoi village) and the nitrogen content of cabbage, which was measured as 1.70×10^{-3} N kg kg^{-1}. The whole area and agricultural area in a watershed were estimated from a 1:25,000 land use map of Tsumagoi Village (Tumagoi Village Office, 2004) by a weighing technique. The area of cabbage field was assumed to be equivalent to the agricultural area because 93% of the agriculture area is covered by cabbage field (Tumagoi Village Office, 2004). The water discharge from a watershed was estimated from the water budget, calculated from the difference between annual precipitation (1664 mm) and evapotranspiration (this was assumed to be 700 mm in the present calculation). Nitrogen export by river (10^6 g N $year^{-1}$ per watershed) was estimated from measured nitrogen concentration in river water and this water discharge.

In Kamagaya city, Chiba prefecture, ground water sampling was conducted from wells along an upland-lowland transect in agricultural area. Orchard and vegetable fields dominate in upland sites, while orchard, vegetable fields and rice paddy in lowland site. Dissolved gas was extracted from sample water in a vial by a headspace method. Gas analysis was made by a GC-system, which enables simultaneous measurement of N_2, O_2, Ar, CO_2 and CH_4 with a sufficient accuracy (Yoh et al., 1998).

Results and Discussion

(1) The balance of fertilizer N input and riverine N export in Tsumagoi highland agricultural region

Concnentration of TDN (total dissolved nitrogen) or nitrate in the whole rivers studied in Tsumagoi showed a variation of more than one order of magnitude ranging from 12 to 223 μ mol L^{-1} and 7 to 195 μ mol L^{-1}, respectively. They showed positive correlations against the percentage of cabbage field coverage in the watershed (data not shown), suggesting that the leaching from cabbage fields is a dominant factor to control the concentration of TDN or nitrate.

Riverine export of TDN is plotted as a function of the estimated nitrogen loading into a watershed in Fig. 1. An excellent linear relationship was found between them with a slope close to 1, implying that the output of nitrogen by rivers is almost equivalent to the input of nitrogen into the watershed. Discharge of inorganic nitrogen proved to be satisfactorily accounted for by the N and hydrological budgets. The results demonstrate a negligible loss of nitrogen within the watersheds, in a striking contrast to previous studies reporting nitrogen removal of large proportions as described above. It is evident that little denitrification is occurring in case of such a sloping highland. The results suggest that nitrogen storage in soil and forests that is presumed in previous studies to be partly responsible for the decreased riverine N fluxes relative to the total anthropogenic nitrogen inputs may contribute little if any.

(2) Importance of lowland as the site of nitrogen removal by denitrification

The study of groundwater showed a distinct difference in NO_3^- concentration along a upland - lowland transect; 930-2000 μ mol L^{-1} (mostly more than the drinking water standard of 10 mg N L^{-1}) in upland site but 0-114 μ mol L^{-1} in lowland sites. Decrease in NO_3^-/Cl^- ratio and decrease in dissolved oxygen concentration were generally observed in lowland sites in comparison with upland sites (Fig. 2). The measurement of dissolved gases showed remarkable increases in relative N_2/Ar ratio in dissolved gases especially in the lowland region, demonstrating N_2 production in

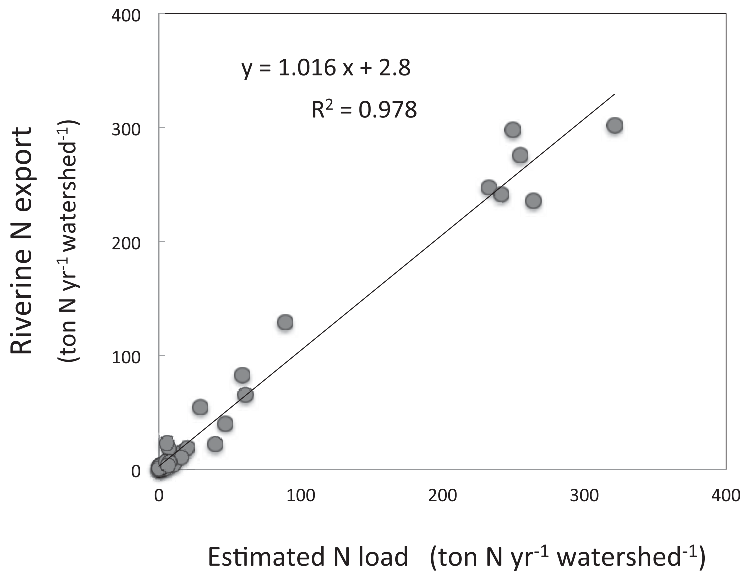

Fig. 1. The relationship between calculated riverine export of dissolved nitrogen and estimated nitrogen loading for watersheds in Tsumagoi highland agricultural region. See text for details to calculate both variables. The equation of linear regression and correlation coefficient is shown in the figure.

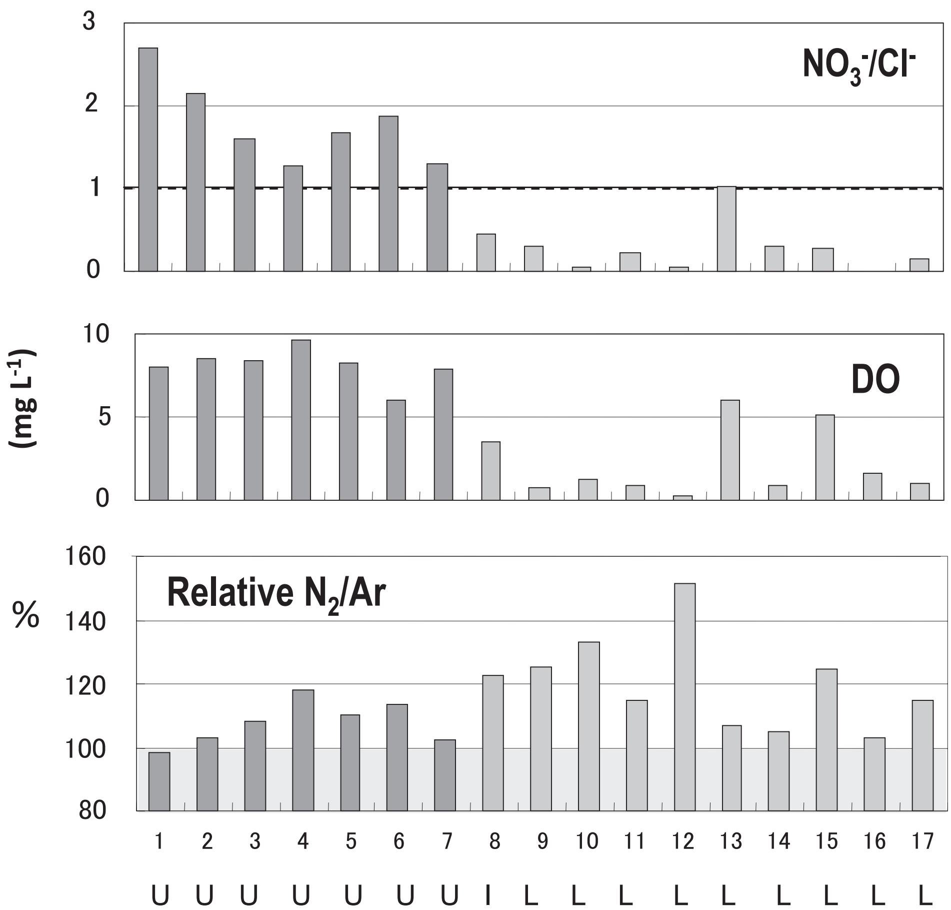

Fig. 2. Change in NO_3^-/Cl^- ratio (top), dissolved oxygen concentration (middle) and relative N_2/Ar ratio in dissolved gases (bottom) along a upland - lowland transect in Kamagaya, Chiba prefecture. Relative N_2/Ar ratio represents the percentage of measured N_2/Ar ratio relative to the theoretical value calculated from in situ temperatures. U, L and I in the figure denote upland sites, lowland sites and intermediate site, respectively.

groundwater. The results demonstrate denitrification largely contributes to the removal of nitrate especially in lowland area, where more humid and deoxygenated condition prevails due to lower position of slope. The prevalence of reductive condition and denitrification has also been observed in riparian zone and in sub-soil deeper than 1m even in forested watersheds (Konohira et al., 1997).

It is reasonable to assume that the ground water at a certain site comes not only from a vertical flow at the same location but also from the upstream area by a lateral flow of ground water in aquifer; namely, it is supplied from the whole upper watershed. In the light of this hydrological connection between upland and lowland, upstream groundwater (sometimes of high NO_3^- concentration) would never go to a river without passing through the lowland zone, where denitrification takes place. It is thus likely that nitrate of elevated concentration in aquifer has a chance to be removed during the process of transport to a surface runoff. The molar ratio of NO_3^- /Cl^- observed in groundwater in the present study was 1.7 and 0.3 in upland sites and lowland sites in average, respectively. On the assumption that the decrease in this ratio in lowlands is due to denitrification and that negligible denitrification is occurring in upland sites, then it is estimated that nitrogen concentration was lowered to 18 % by denitrification, equivalent to the ratio of observed riverine N export to calculated N input in the river basin of 16% to 25% (Howarth et al., 1996; Caraco and Cole, 1999; Howarth et al., 2006).

In addition to a lateral topographical importance addressed above, a longitudinal aspect in landscape is of another significant implication regarding to the nitrogen sink in lands. The longitudinal section of a river, and accordingly the land surface, generally has a shape approximated by an exponential curve. A significant drop in NO_3^- concentration has been observed in stream waters in forest areas of lower elevation in Tama River system, where dissolved Mn, NH_4^+ and the evidence of sulfate reduction are also found in stream waters indicative of reductive condition in these areas (Yoh et al., 2004). Increase in dissolved Fe concentration has also been shown in streams of lower reaches in a forested watershed of the Amur River basin (Yoh et al., 2010). It is thus likely that reductive condition and denitrifying zone would be usually prevailing under the soil in lower reaches, probably according to a gentle slope and a shallow ground water table.

The results raised here suggest that nitrogen leached out from agricultural lands could be substantially removed by denitrification in the river basin in general, which has not been unambiguously recognized. Further systematic researches are required to know the actual quantitative importance of denitrification and the boundary conditions regulating this process to contribute to nitrogen removal during the discharge process.

Acknowledgement

The author thanks Ms. S. Arai, Mr. C. Moon, and Mr. W. Shintani for their works to contribute greatly to the results presented in this paper.

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